

The Individual Adsorption of Carbon Dioxide and Sulphur Dioxide by Y Zeolites

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The sulphur dioxide and carbon dioxide individual adsorption capacities of the Y zeolites, whose structure was confirmed by XRD, were determined at temperatures from 25 to 200°C and concentrations in the feeding gas from 0.92% - 5.04% for SO₂ and 2.95% - 11.43% for CO₂ (% vol.). The effect of the adsorption – desorption – thermal regeneration cycles on the adsorption capacity of the Y zeolites was determined too. The presence of water vapors increases the adsorption capacity for SO₂ at high temperatures. Y zeolites, good adsorbents for sulphur dioxide found in residual gases, also have a great carbon dioxide adsorption capacity even at a temperature of 190°Celsius, or when being confronted with low concentrations, 2.95%, proving a very balanced stability at cycles of adsorption - desorption - regeneration. The mechanisms proposed for the adsorption of sulphur dioxide and carbon dioxide by the Y zeolites are supported by the IR spectra.

Keywords: Y zeolites, sulphur dioxide, carbon dioxide, adsorption, mechanism of adsorption.

Residual gases that appear especially after burning processes of fuels (coals or oil fractions), contain beside water carbon dioxide, sulphur dioxide, nitrogen, oxygen, etc in various proportions [1-3]. Therefore, when burning the typical brown coal (it has about 0.2 kgC/Kg brut coal and 0.006 kgS/kg brut coal as burning elements) the dry residual gas contains as volumetric percentages 0.149% sulphur dioxide, 12.76% carbon dioxide, 6.6% oxygen, 80.49% nitrogen. Looking to the environment rules which imposes no more than 50 ppm SO₂ for gasses dispersed in the atmosphere we find out that the removal of SO₂ is an important requirement.

The gravimetric composition of the brown coal from Rovinari.

The SO₂ removal and depollution of residual gases resulting from thermo electrical plants through adsorption by a fixed bed adsorbent is a potential alternative to the conventional technologies based on wet or dry cleaning. The later ones are high operation cost technologies with a low SO₂ removal efficiency and they raise the problem of waste disposal [4]. The adsorption processes may occur with high removal rates but they require large volumes of adsorbent and high energy consumption for the adsorption regeneration. These problems can be solved using an adsorbent material with a high sulfur dioxide adsorption capacity. In the SO₂ adsorption process a large variety of adsorbents have been tested [5-15] from which the natural or synthetic zeolites seem to have the highest activity. The presence of CO₂ in the gasses with SO₂ content, requires, concerning his adsorption on a given sorbent, the same attention as SO₂. With respect to this problem of SO₂ removal from gasses with high CO₂ content the paper aim is to analyze the individual and simultaneous species adsorption on a zeolite sorbent following a better knowledge of inter phase equilibrium and of solid-species interaction mechanisms. This characterization of individual species adsorption using the experimental investigation based on differential sorption in a zeolites fixed bed is presented in this study. The zeolite samples

were supplied by INCERP Ploiesti, Romania. The structures of the Y zeolites were identified by XRD (Bruker D5005, CuK_α) measurements.

Experimental part

Being found next to sulphur dioxide, more abundant than it in the residual gases and contributing massively to the greenhouse effect, the analysis of carbon dioxide adsorption [16-23] by the HY - 928 and NaY - 1633 zeolites, besides that of sulphur dioxide, is also necessary. Due to the similarities between SO₂ and CO₂ molecules we expect to have strong similarities at their adsorption equilibrium on the same sorbent, especially our checked zeolites. The experimentally tested zeolites have a crystal structure with specific groups which can control the species sorption. Due to the crystalline structure of zeolite here shown by the X-ray diffraction pattern displayed in figure 1, the sorption of SO₂ or CO₂ can be explained by its interaction with the ones of zeolite crystal zones.

The study of carbon dioxide adsorption capacity in dynamic regime, after achieving the adsorption-desorption equilibrium state, considering the temperature at which the adsorption occurs was taken into account, as well as the concentration of carbon dioxide in the adsorbed gaseous flux and the stability of the adsorbent. The laboratory equipment used in the experiment is schematically presented in figure 2. The SO₂ and CO₂ adsorption was carried out into a fixed bed reactor using roughly 2-3 g (5cm³) of zeolite and inert (fig. 2).

The utilised gas was a synthetic mixture of nitrogen and sulfur dioxide or carbon dioxide. Beforehand the zeolites were thermally treated for one hour at 120°C, and after that another hour at 400°C in a nitrogen stream. The adsorption temperature was in the range of 25-200°C. The desorption was carried out thermally (400°C) in a nitrogen stream. The adsorbed quantity of sulphur dioxide was established by iodometric titration, and the measurement of carbon dioxide quantity is conducted after keeping it in 50 mL solution 2N of NaOH in the bubble flask, using the

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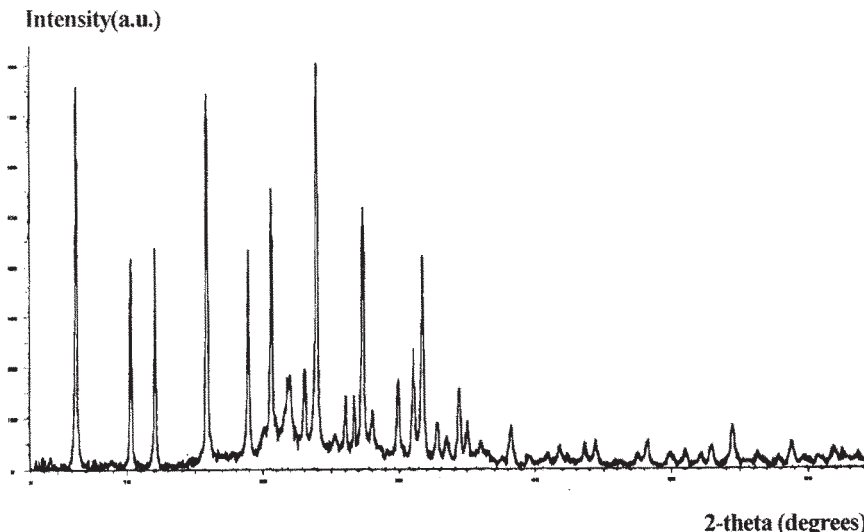


Fig.1. X-Ray diffraction patterns of the Na Zeolite used as adsorbent

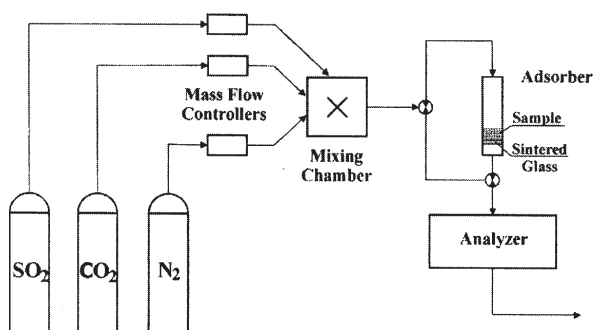


Fig. 2. Laboratory plant for sulphur dioxide or carbon dioxide adsorption

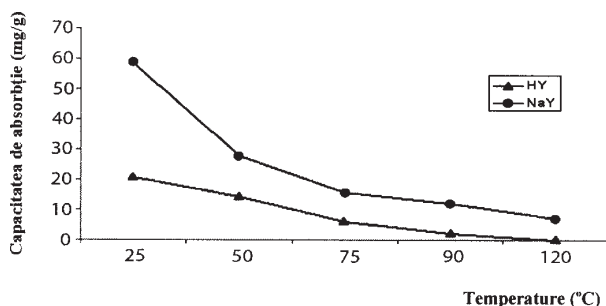


Fig. 3. The influence of temperature on the SO₂ adsorption of the Y zeolites (flow velocity of 0.6 m/s and a sulphur dioxide concentration of 1,83 % v/v)

2-theta (degrees)

value becomes zero. The high values for the adsorption capacities of the zeolites at low temperatures are supposed to be the result of both the physical adsorption and the chemisorption, the former being in this case predominant [5,25,26].

In the case of temperature effect on the CO₂ adsorption capacity the flow rate has been kept at flow velocity of 0.6 m/s (gas flow rate is 131 mL/min) whereas the CO₂ concentration within the N₂ flux is 8.6% v/v. Figure 4 synthesizes these measurements.

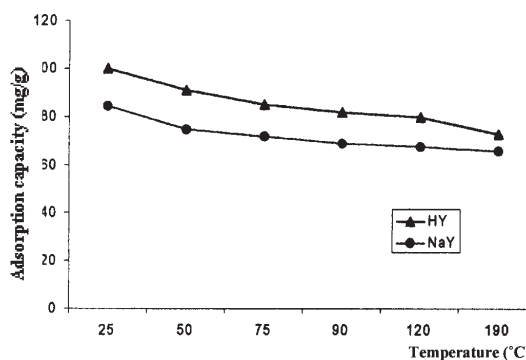


Fig. 4. The influence of temperature on the CO₂ adsorption of the Y zeolites (flow velocity = 0.6 m/s and a carbon dioxide concentration of 8.6 % v/v)

Warder method [24]. The adsorbent regeneration was carried out at 400°C for 30 min in nitrogen flow.

Results and discussions

Influence of Temperature on the Adsorption Capacity

The industrial residual gases have a temperature exceeding that of the environment. Therefore it is interesting to study the influence of the temperature over the adsorption capacity, measured as mg of adsorbed gas per 1 gram of zeolit. In the experiments showing the temperature effect (fig.3) on adsorption capacity the sulphur dioxide concentration in nitrogen is 1.83% (%vol.) and the gas flow corresponds to the fictive velocity of 0.6 m/s (gas flow rate of 131 mL/min). Thus, as expected, [5,10,11] it was experimentally observed that the adsorption capacity decreases with temperature increasing in the case of both zeolites, HY and NaY, the adsorption capacity for NaY always being higher.

The NaY zeolite maintains high adsorption capacity values in the temperature range of 75-100°C but when the temperature exceeds this value, its adsorption capacity

By analysing the results, a few interesting things can be noticed in concordance with the data from the specialized literature [2,3,27-31]. Thus, increasing the temperature, the zeolites' capacity of adsorbing carbon dioxide decreases, maintaining significant values even at 190°C. Furthermore, the HY zeolite presents higher values of adsorption capacity on the entire scale of temperature, compared to the NaY zeolite, although the diminution of the adsorption capacity is more severe for HY zeolite (26.87 units) as compared to NaY zeolite (18.47 units) for the range 25-190°C.

Influence of the Concentration over the Adsorption Capacity

The sulphur dioxide content in the residual gases fluctuates depending on the emission source. In figure 5 are showed the adsorption isotherms of Y zeolites obtained when the sulphur dioxide content in the feeding gas was altered. The slope of these isotherms varies suddenly in the range of low concentration and after that the adsorption

capacity is only slightly influenced by the concentration. Other authors [3,5,10,15,32,33] also report an increase in the adsorption capacity with the increase of sulfur dioxide concentration in gases. This behavior could be explained by the accumulation of sulphur dioxide in a condensed state [5].

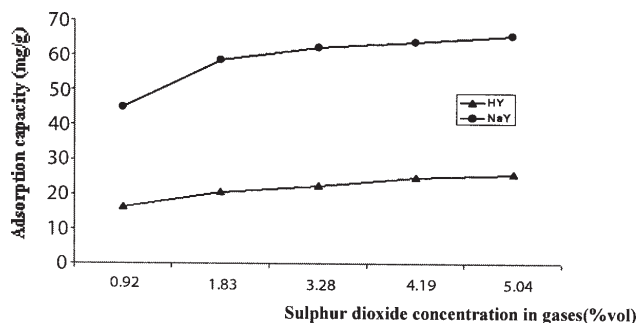


Fig. 5. Adsorption isotherms for SO_2 on Y zeolites at a flow velocity of 0.6 m/s and a temperature of 25°C

It can also be observed from figure 5 that, as it was expected, that the NaY zeolite has the highest adsorption capacity for the whole range of concentrations studied.

The isotherms of adsorption of carbon dioxide by the Y zeolites were established at 25°C using a synthetic gas that contains carbon dioxide and nitrogen in different amounts with a flow rate in the plant of a 131 mL/min. The resulting data are gathered in figure 6, which shows us an increase of the adsorption capacity for CO_2 of the 2 zeolites.

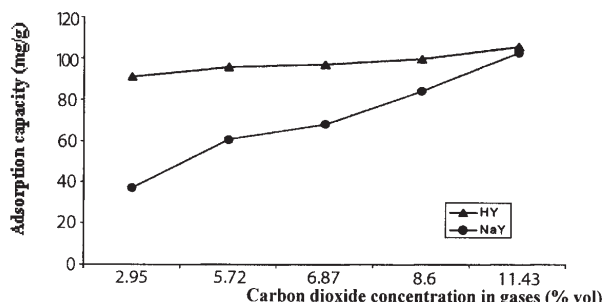


Fig. 6. Adsorption isotherms for CO_2 on Y zeolites at a flow velocity of 0.6 m/s and a temperature of 25°C

This increase is slower for the HY zeolite and more obvious for the NaY zeolite. It must be mentioned that at high concentrations of carbon dioxide in the supply gas, the difference between the adsorption capacities of the two zeolites decreases intensely, from 53.9 units for the concentration of 2.95% carbon dioxide to 3.91 units for the concentration of 11.43% carbon dioxide in favour of the HY zeolite.

The fact that for high amounts of carbon dioxide in the synthetic gas the adsorption capacities almost become equal could be explained by the fact that increasing the carbon dioxide concentration, it “stays” onto the zeolite after the superficial saturation in a condensed form, followed by a slow increase in the mass of carbon dioxide retained through a possible process of solvating the gaseous carbon dioxide in condensed substance.

Regeneration and Stability of the Adsorbent

A measure of the effectiveness of using an adsorbent in the process of adsorbing carbon dioxide from a gaseous mixture is the stability of the adsorbent in the adsorption – desorption – regeneration cycle, and also the

accomplishing of the regeneration as simply as possible in a short period of time and with reduced expenditures. In order that SO_2 and CO_2 should be absorbed by Y zeolites the method of thermal regeneration was adopted, by maintaining the zeolite at a temperature of 400°C for 30 min in a current of nitrogen. It has been shown in the literature [13] that some zeolites do not lose their activity even after 2000 such cycles operated under industrial conditions. As it can be seen from figure 7, the HY and NaY zeolites do not significantly alter their activities after 20 adsorption-desorption-regeneration cycles operated under identical experimental conditions like 25°C, 1.82% SO_2 in N_2 , gas flow 131 mL/min.

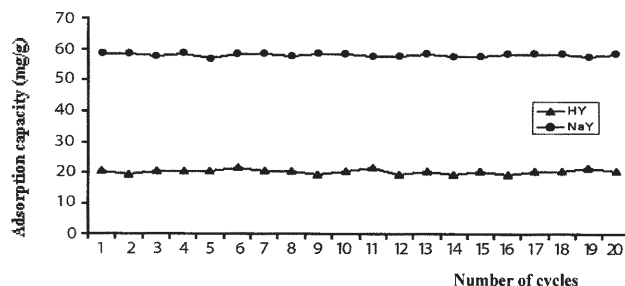


Fig. 7. Influence of the number of adsorption-desorption-thermal regeneration cycles on the adsorption capacity of the zeolites HY and NaY

Practically, after 20 adsorption – desorption – regeneration cycles, working with a synthetic gas containing 8.6% CO_2 and 91.4% N_2 , at 25°C and with a flow of 131 mL/min, the two zeolites have a constant behaviour concerning CO_2 adsorption, maintaining their adsorption capacities (table 1).

However it is possible that on adsorption of a mixture of SO_2 and CO_2 , in the presence of water vapors and at higher temperatures the activity of these adsorbents will be altered [34-36]. Furthermore, measurements have proved that the presence of water vapors improves the adsorption capacity for SO_2 by 0.6 % at 90°C and by 35% at 120°C.

Mechanism of Adsorption

In order to obtain some information about the adsorption mechanism on the Y zeolite, the sulphur dioxide adsorption was investigated using IR spectroscopy. The most striking feature of the SO_2 spectrum is a pair of absorption bands representing S = O vibrations. These occur in the gas phase at 1360(V_3) and 1151 cm^{-1} (V_1) and are also found in the spectrum of SO_2 adsorbed at room temperature and low pressure at 1330 cm^{-1} and 1140 cm^{-1} , values similar to those observed for liquid SO_2 [37].

The IR spectra of the NaY zeolite with and without adsorbed sulphur dioxide are shown in figure 8.

An absorption band at 1325 cm^{-1} , corresponding to adsorbed SO_2 , can be easily seen. The accompanying band at 1150 cm^{-1} is not visible because of the background absorption of the zeolite in this region. A pair of absorption bands at 1440 cm^{-1} and 1550 cm^{-1} that might be the V_3 and V_1 vibrations of perturbed SO_2 molecules can also be seen [37]. Hence, the spectrum shows two forms of adsorbed sulphur dioxide, physisorbed and chemisorbed. Deo [37] suggested that SO_2 adsorption results in the disappearance of the high frequency OH vibration and the appearance of a broad band at 3500 cm^{-1} due to hydrogen bonded OH. Obviously the SO_2 is adsorbed by hydrogen bonding to surface hydroxyl groups, as shown in figure 9. This fact was not visible in the present study because of the background absorption of the zeolite in this region of the spectrum.

Number of cycles	The adsorption capacity (mg _{sulphur dioxide} /g _{zeolite})	
	HY	NaY
1	99,98	84,47
2	99,98	83,12
3	98,28	84,30
4	99,98	84,47
5	98,28	84,30
6	98,28	84,47
7	99,98	84,30
8	99,80	84,30
9	99,98	83,12
10	98,28	84,47
11	99,98	84,47
12	98,28	84,47
13	99,98	84,47
14	99,98	83,12
15	98,28	84,47
16	99,98	84,47
17	99,98	84,47
18	99,98	84,30
19	98,28	83,12
20	98,28	83,28

Table 1
THE EFFECT OF THE NUMBER OF ADSORPTION -
DESORPTION - REGENERATION CYCLES
ON THE ADSORPTION CAPACITIES OF Y ZEOLITES
(FLOW VELOCITY 0.6 M/S, CO₂ CONCENTRATION
8.6% V/V, TEMPERATURE 25°C)

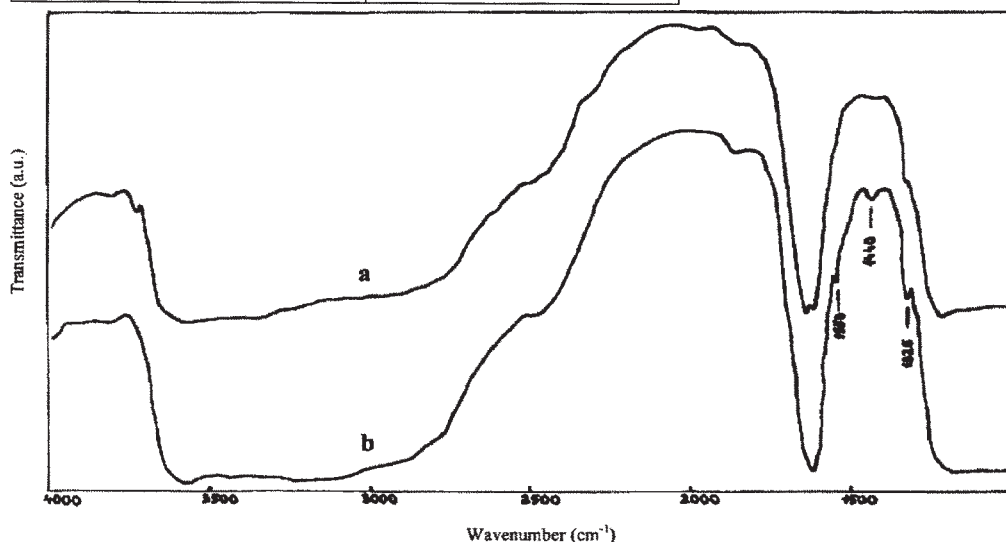


Fig. 8. IR Spectra of NaY zeolite without (a) and with (b) adsorbed SO₂

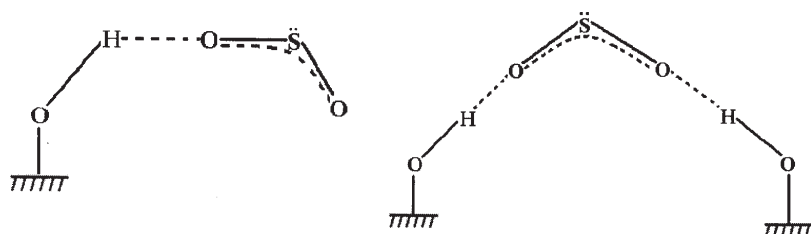


Fig. 9. Methods of interaction between sulphur dioxide and the zeolite

Regarding the mechanism of carbon dioxide adsorption there is a series of detailed research carried out especially on zeolites. Thus, starting from the study of the phenomenon of carbon monoxide adsorption by the Na-ZSM-5 zeolite [38], which suggests that, more than one carbon monoxide molecule can be absorbed by the same cation of the zeolite, the researchers concluded that two molecules of carbon monoxide can be coordinated by the same Na⁺ ion from the NaY zeolite [39-41]. Subsequently, in a research from 2000, it was suggested [42] and then confirmed [27] that, depending on the pressure of the

adsorbed gas at a state of equilibrium, the sodium ions (Na⁺) from the Na-ZSM-5 zeolite can coordinate one or two molecules of carbon dioxide according to the equations below:



The most recent evidence, which supports the formation of coordinated species Na(CO₂)_n⁺, where n can be equated

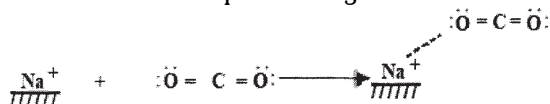
with 1 or 2, are derived from the volumetric adsorption measurements which show that the number of mols of carbon dioxide adsorbed far exceeds the number of centres of adsorption Na^+ from Na-ZSM-5.

Analysing the evolution of the series of zeolitic adsorbents M^+ -ZSM-5 where M^+ is in turn Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Bonelli demonstrates that the adsorbed carbon dioxide molecules interact not only with the M^+ cations but also with the nearest oxygen anions. The interaction with the cations decreases in intensity from Li^+ to Cs^+ , while the interaction with the oxygen anions increases from Li^+ to Cs^+ . The dual nature of the interaction is proved through the analysis of the IR spectra and could not have been anticipated based only on the analysis of the $\text{CO}_2/\text{Na-ZSM-5}$ system; it has been set up by a combined analysis of the IR spectra for the $\text{CO}_2/\text{M}^+\text{-ZSM-5}$, where M^+ was in turn Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ .

Carbon dioxide molecules are driven to interaction by the combined electric field of neighbouring cations and anions, on the surface of the zeolite. It must be stressed that the carbon dioxide interaction with the oxygen anions is never strong enough to facilitate the formation of carbonate species as it is in the case of carbon dioxide adsorption by the Na-A zeolites, $\text{M}^+\text{-ZSM-5}$ and faujasit[27,43,44].

Taking the evidence provided by the specialized literature as a starting point, it can be inferred that, for carbon dioxide to be adsorbed by the Y zeolites, the following mechanisms can be suggested:

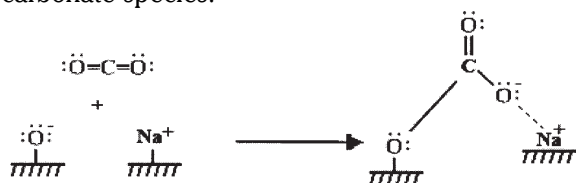
a. Carbon dioxide adsorption through coordination on Na^+ :



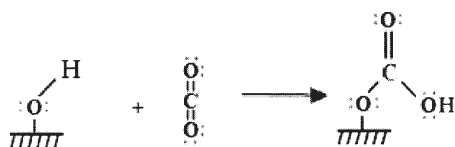
b. Carbon dioxide adsorption through the interaction with oxygen anions:



c. Carbon dioxide adsorption through the interaction with Na^+ : and the neighbouring oxygen anion with the formation of carbonate species:

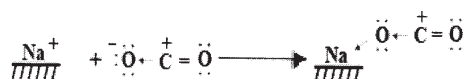


d. Interaction with hydroxide groups belonging to the zeolites surface, shown through IR spectra [27, 43]:

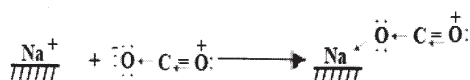


Taking into account the limit structures of carbon dioxide, the following mechanisms are suggested:

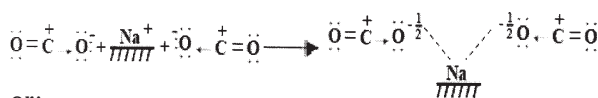
- the coordination of a carbon dioxide molecule at a sodium ion:



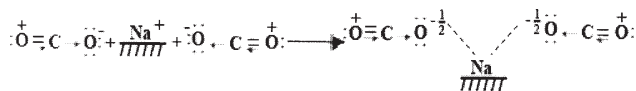
or:



- the coordination of the two carbon dioxide molecules at a sodium ion:



or:



Conclusions

The experiments carried out to study the sulphur dioxide and carbon dioxide adsorption by the zeolites suggest the following conclusions:

- the sulphur dioxide and carbon dioxide adsorption capacities of Y zeolites decrease with the increase in temperature but can meet high values even at 190°C which suggests a powerful interaction between the zeolite and the carbon dioxide;

- the SO_2 and CO_2 concentration respectively in the sintetic gas influence the adsorption capacity of the zeolites;

- increasing the temperature at which the adsorption occurs, it can be noticed, as was expected, that the zeolite's adsorption capacity of the two gases decreases.

- after adsorption and desorption, the zeolite regeneration can be easily achieved through a thermal process;

- the HY and NaY zeolites prove to have a good constancy in the adsorption – desorption – regeneration cycles.

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